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I. THE MECHANISM OF THE BASIC HYDROLYSIS OF DIBROMOCHLOROMETHANE AND DIBROMOFLUOROMETHANE

II. AN ATTEMPTED SYNTHESIS OF CYCLOBUTENE

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I. THE MECHANISM OF THE BASIC HYDROLYSIS OF DIBROMOCHLOROMETHANE AND DIBROMOFLUOROMETHANE

II. AN ATTEMPTED SYNTHESIS OF CYCLOBUTENE

Approved:

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SUMMARY

Evidence is presented to show that the basic hydrolysis of dibromofluoromethane and dibromochloromethane is through a trihalomethyl carbanion and carbon dihalide intermediate rather than through a mechanism involving S_N2 attack of water molecules upon the trihalomethyl anion or by a S_N2 attack of hydroxide ions upon the haloform.

CHAPTER I

INTRODUCTION

Hine and Dowell have shown that the basic hydrolysis of chloroform is through a carbon dichloride intermediate (1). The proposed mechanism is as follows:

$$\text{I.}\quad CHX_3 + OH^- \rightleftharpoons CX_3^- + H_2O \qquad \text{(fast)}$$

$$CX_3^- \longrightarrow CX_2 + X^- \qquad \text{(slow)}$$

$$CX_2 \xrightarrow[OH^-,H_2O]{} CO + HCO_2^- \qquad \text{(fast)}$$

The present study was undertaken to determine if the same mechanism would explain the hydrolysis of dibromochloromethane and dibromofluoromethane.

Data on the base-catalized deuterium exchange of dibromochloromethane supports this mechanism (2). The rate of carbanion formation of dibromofluoromethane, predicted from the rates of exchange of deuterochloroform (3), deuterobromoform, deuterodichlorofluoromethane (4), and deutero-

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1 J. Hine and A. M. Dowell, Jr., J. Am. Chem. Soc., 76, 2688 (1954).

2 R. H. Sherman and R. B. Bernstein, J. Am. Chem. Soc., 73, 1376 (1951).

3 J. Hine, R. C. Peek and B. D. Oakes, J. Am. Chem. Soc., 76, 827 (1954).

dichlorobromomethane (4), also supports this mechanism. Replacement of a chlorine atom of chloroform with a bromine atom increases the rate of deuterium exchange by six times. Replacing three chlorine atoms of chloroform with bromine atoms increases the rate of deuterium exchange one hundred twenty times. It appears logical that an increase of twenty-four times would be expected when the two chlorine atoms in dichlorofluoromethane are replaced by bromine atoms. The carbanion formation rate of dichlorofluoromethane is 1.5×10^{-4} liters per mole per second. The predicted carbanion formation rate of dibromofluoromethane is 36×10^{-4} to 54×10^{-4} liters per mole per second. This is greater than the hydrolysis rate of 27.8×10^{-4} liters per mole per second at 0°. The deuterium exchange rates of both compounds are faster than the hydrolysis rates, as required by this mechanism.

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4 N. W. Burske, unpublished work, Georgia Institute of Technology.

CHAPTER II

METHOD OF ATTACK

The hydrolysis of the two haloforms studied was found to be second order, first order in hydroxide ion, and first order in haloform concentration.

The most reasonable mechanisms that predict such kinetics are mechanism I (page 1) and mechanisms II and III below.

II The S_N2 mechanism:

$$CHX_3 + OH^- \longrightarrow HOCHX_2 + X^- \qquad \text{(slow)}$$

$$HOCHX_3 \xrightarrow[H_2O,\ OH^-]{} CO + HCO_2^- \qquad \text{(fast)}$$

III The S_N2 attack by H_2O on the CX_3 anion:

$$CHX_3 + OH^- \rightleftharpoons H_2O + CX_3^- \qquad \text{(fast)}$$

$$CX_3 + H_2O \rightleftharpoons H\text{-}\overset{\oplus}{O}(H)\text{-}\overset{\ominus}{C}X_2 + X^- \qquad \text{(slow)}$$

$$H\text{-}\overset{\oplus}{O}(H)\text{-}\overset{\ominus}{C}X_2 \xrightarrow[H_2O,\ OH^-]{} CO + HCO_2^- \qquad \text{(fast)}$$

Mechanism III appears to be less likely than mechanism I. Mechanism III requires that the negatively-charged end of the H-O dipole of the water molecule attack the trihalomethyl anion rather than a neutral haloform molecule.

Table 1. Relative Rates of Reaction of Haloforms with Hydroxide Ion in 66 2/3 Per Cent Aqueous Dioxane. (5)

Halide	Rate in liters per mole per second at 35.7°
$CHCl_3$	0.034
CH_2Cl_2	0.00018 (6)
CCl_4	0.000005 (6)
$CHBr_3$	0.15
CH_2Br_2	0.00007
CBr_4	0.01

5 J. E. Singley, Jr., M. S. Thesis, Georgia Institute of Technology, 1952, p. 5.

6 J. Hine, J. Am. Chem. Soc., 72, 2438 (1950).

Table 2. Per Cent Completion of the Reaction of Some Chloro-substituted Methanes with Ethoxide Ion at 90° at the End of Thirty Minutes. (7)

Halide	Per Cent Completion
CH_2Cl_2	8
$CHCl_3$	84
CCl_4	35

7 P. Petrenko-Kritschenko and V. Opotsky, Ber., 59B, 2131 (1926).

Mechanism II appears to be less likely than mechanism I. Tables 1 and 2 show that the haloforms are more reactive toward base than are methylene halides or tetrahalomethanes. Since halogen atoms decrease S_N2 activity of carbon atoms to which they are attached, the rate of basic hydrolysis would decrease as the number of halogen atoms increased, if mechanism II were operating.

Work on the effect of added salts upon the rate of solvolysis of p,p'-dimethylbenzylhydryl chloride in aqueous acetone has shown that the loss of the chloride ion to form the carbonium ion is reversible and that the rate is specifically reduced by the addition of chloride ion (8). This is termed a "mass law effect".[1] The possibility of its observation increases with increased stability of the carbonium ion.

The second step of mechanism I produces a carbon dihalide intermediate from the S_N1 decomposition of a trihalomethyl carbanion. Since the carbon atom of this intermediate is surrounded by six electrons, it is possible to treat this intermediate as a special type of carbonium ion. A mass law effect on this carbonium ion is possible in mechanism I. A mass law effect would not be expected in mechanism II or mechanism III. Specifically, the presence of iodide ions or bromide ions could lower the rates of hydrolysis of dibromofluoromethane and dibromochloromethane, if these

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8 L. C. Bateman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 1940, 960, 974.

[1]For a discussion of mass law effect, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N. Y., 1953, pp. 360 - 371.

haloforms proceed through mechanism I.

Therefore, the rates of basic hydrolysis in the presence of several added salts were determined. Sodium nitrate, sodium perchlorate, sodium fluoride, sodium bromide, and sodium iodide were used at concentrations of 0.08 to 0.09 N.

Since the rates of hydrolysis of dibromochloromethane were definitely lower in the presence of sodium iodide and sodium bromide than in the presence of the three inert salts, sodium perchlorate, sodium nitrate and sodium fluoride, it was apparent that bromide ions and iodide ions were intervening. In addition, the rate constant in the case of the iodide fell with time, a behavior lending support to the theory of intervention of both bromide and iodide ions with the chlorobromomethylene intermediate.

The rates of hydrolysis of dibromofluoromethane were the same within the experimental error for all five salts. Any intervention by the iodide ion and the bromide ion with the carbon dihalide intermediate was of less magnitude than the experimental error.

CHAPTER III

EXPERIMENTAL

Kinetic Runs

The kinetic runs at 40° C. were made in a large constant temperature water bath. The temperature was constant to within 0.1° C.

The runs at 0° were made in an insulated icebox constructed from a five gallon can with one side cut out. It was supported in a plywood box in such a way as to allow for approximately 1½ inches of sawdust insulation on all sides. An insulated top was provided. During the runs, the box was kept filled with a slurry of cracked ice and water. The temperature was constant to within 0.1°.

The multiple flask technique was used for the determination of the rate of basic hydrolysis of dibromofluoromethane because of the low solubility of the haloform in water and its high vapor pressure at this temperature. Into each of several (generally seven to sixteen) 100 ml. volumetric Pyrex flasks was pipeted 80 ml. of 0.1 N salt solution. The flask was then swept out with nitrogen, stoppered, and placed in the constant temperature bath for at least one-half hour. One-fourth of a milliliter of pure haloform at room temperature was added to each flask by means of a hypodermic syringe that was found to deliver 0.250 ml. - 0.00075 ml. (average deviation). The flask was re-stoppered, and the solution of the

haloform completed by vigorous shaking for about five minutes. The weight of the dibromofluoromethane was calculated from the density of the haloform at the temperature delivered. After at least thirty minutes the reaction was started by pipeting 20 ml. of standard sodium hydroxide at 0° into the flask. The entire contents of a single flask were used for a single point. A zero point was run as soon as possible; the elapsed times, the concentrations and back titer of base were corrected to this zero point. To take a single point, the flask was removed from the bath, wiped dry with a towel, and the contents of the flask were quantitatively transferred to a 200 ml. titrating beaker containing a measured volume of a standard acid (an excess of hydrochloric or perchloric acid to stop the reaction). The excess acid was back titrated with standard sodium hydroxide with phenolphthalein. The time for the reaction was taken as the time between the midpoint of the addition of sodium hydroxide and the midpoint of the emptying of the volumetric flask into the beaker. The rate constants were calculated for each point from the following integrated second order rate expression:

$$k = \frac{2.303}{t\,[(3 + f)\,a + b]} \log \frac{b}{b - (3 + f)\,x} \cdot \frac{a - x}{a}$$

where t = the time in seconds,
a = the initial concentration of haloform,
b = the initial concentration of base,
f = the fraction of haloform yielding formate ion,

x = the change in concentration of haloform,
k = the rate constant.

In the kinetic runs of dibromochloromethane the multiple flask technique was modified somewhat. In order to provide more uniform solutions, 0.50 ml. of the dibromochloromethane was dissolved in 500 ml. of the desired salt solution. The solution was accomplished by intense shaking for one hour. Nitrogen gas from a cylinder was used to force the haloform-salt solution into an 80 ml. pipette, which was then drained into the 100 ml. volumetric flask as described above. This method of filling the flasks also reduced loss of haloform, because no suction was applied to the solution. The procedure was not changed after this. Only 10 ml. of sodium hydroxide solution was added to start the reaction in the hydrolysis of dibromochloromethane.

In some runs the 80 ml. pipette was replaced by a 75 ml. pipette.

Certain points were considered statistically unreliable. The rate constant for any of these points differed from the average rate constant of the other points in the same salt solution by more than four times the average deviation of the other points.

Determination of the Factor f

The factor f is defined as the fraction of the haloform undergoing hydrolysis that yields formate ion. The products of the basic hydrolysis of haloform are carbon monoxide and formate anion.

$$CHX_3 + 3NaOH \rightarrow 3NaX + CO + 2H_2O$$

$$CHX_3 + 4NaOH \rightarrow 3NaX + NaHCO_2 + 2H_2O$$

It is evident that

$$\frac{\text{moles of hydroxide used}}{\text{moles of haloform used}} = 3 + f.$$

The moles of hydroxide were determined by the same titrations used in the kinetic runs as described above. The moles of haloform were determined by titration against silver nitrate solutions, after the hydroxide titrations.

In the determination of f for dibromofluoromethane, the procedure used was identical with that used in the kinetic runs, except that air-free distilled water was used in place of the salt solution. After the back titration using phenolphthalein, 1.0 ml. of fluorescein per 100 ml. of solution was added to the titrating flask. Silver nitrate was then titrated against the bromide ion in solution. The silver nitrate was standardized against standard sodium bromide.

In the determination of f for dibromochloromethane, the procedure as described above was used with the following change: dichlorofluorescein was used as the indicator, as fluorescein is not satisfactory for the determination of chloride.

A different experimental procedure was also used to determine f for dibromofluoromethane. Several 100 ml. volumetric flasks, containing

0.25 ml. of haloform and two drops of phenolphthalein dissolved in 80 ml. of distilled, nitrogen-free water, were placed in the constant temperature bath. At the end of one hour, a volume of standard sodium hydroxide at 0° was pipetted into the reaction mixture. When the color of the phenolphthalein had almost disappeared, the reaction mixture was washed into a measured amount of standard acid and titrated for chloride ion with dichlorofluorescein as an indicator. The value of $\underline{f}$ was identical with that found in the previous method.

Constant Temperature Correction

When it was noted that the calculated rate constants of hydrolysis for dibromofluoromethane fell in a roughly exponential manner, it was believed that this was due to a temperature effect. To determine the magnitude of the temperature effect and to correct the rate constants, the following procedure was initiated.

A curve of temperature of the reaction solution against time was found using the following apparatus. Two iron-constantan thermocouples with lead wires of eighteen inches were constructed. The two constantan wire ends were connected. One iron wire end was connected to a Leeds-Northrup Galvanometer with a sensitivity of 0.46 microvolts per mm., and a resistance of 16 ohms. The remaining iron wire was connected to a resistance box. The resistance box was composed of one 600 ohm resistor, one 50 ohm potentiometer, and one 175 ohm potentiometer - all of which were connected in series. The remaining terminal of the box was

connected to the galvanometer. During all experimental runs, the galvanometer and resistances were covered with a cardboard box to prevent parasitic electro-motive forces caused by drafts.

The galvanometer was calibrated to read 10° C. for full scale deflection. When both thermocouples were placed in a slurry of ice and water, the galvanometer adjustment knob was set so that the scale read 0.0° C. One of the thermocouples was removed and placed in a thermos jar containing water and a thermometer. The two potentiometers were adjusted until the scale reading was equal to the temperature of the thermometer.

During experimental runs, one thermocouple was immersed in a slurry of ice water and the other thermocouple was suspended in the reaction solution. The experimental runs were performed in the manner previously described. The temperature of the reacting solution was recorded at intervals of one minute or less. The temperature effect found was attributed to heat of solution, heat of reaction and warming of the pipette during experimental operations. The corrected unintegrated second order rate equation has the following form:

$$\frac{dx}{[a - x]\,[b - (3 + f)\,x]} = k_o \exp - \frac{H(T_o - T)}{RT_oT} \cdot dt$$

where a, b, x, t, and f represent the same quantities previously listed, and

k_o = the corrected rate constant at 0° C.,
T_o = the temperature of the bath in degrees Kelvin,
T = the true temperature of the reacting solution, in degrees Kelvin at time, t,
H = the energy of activation per mole, and
R = the universal gas constant.

It is obvious that the previously calculated, uncorrected rate constant, k, is related to the corrected rate constant, k_o, by the expression:

$$\frac{k}{k_o} = \frac{t + \int \exp - \frac{H(T_o - T)}{RT_oT} \, dt}{t}$$

The expression on the right is called the correction factor. The integral in this equation was evaluated by graphical methods for several values of the parameter, H, and the corrected rate constant was calculated for each point of the reaction. The smallest average deviation of corrected rate constants for the five salt solutions was obtained when the value of H was taken as 27.7 kilocalories per mole. These rates are listed in Table 3. Since this value is sensitive to any type of drift error, a value of H of 26.5 kilocalories per mole, obtained from the average heat of activation of seven haloforms found by Dowell (9), was

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9 A. M. Dowell, Jr., Ph. D. Thesis, Georgia Institute of Technology, p. 43.

Table 3. Value of Heat of Activation Leading to Minimum Average Deviations of Corrected Rate Constants.

Salt	Heat of Activation In Kilocalories Per Mole	Rate Constant $k \times 10^5$ In Liters Per Mole Per Second
NaF	26.5	276
$NaNO_3$	31.4	287
NaBr	27.6	275
NaI	26.5	266
$NaClO_4$	26.5	277
Average	27.7 ± 1.5	

Table 4. Rate Constants of Dibromofluoromethane in the Presence of Various 0.08 N Salts.

Salt	$k \times 10^5$ In Liters Per Mole Per Second	Average Deviation
NaF	276	8
$NaNO_3$	295	6
NaBr	276	3
NaI	266	1
$NaClO_4$	277	3
Average	278	6

Table 5. Correction Factors at Various Times

Time Seconds	Ratio k/k_o
00	1.285
100	1.260
200	1.240
300	1.223
400	1.208
500	1.194
600	1.181
1200	1.129
1800	1.112
2400	1.082
3000	1.070
3600	1.062
4200	1.055

used to obtain the rate constants listed in Table 4. These rate constants are believed to be more reliable. The correction factors for various times at a value of H of 26.5 kilocalories per mole are listed in Table 5.

Preparation and Purification of Reagents

Dibromofluoromethane.— Dibromofluoromethane was prepared by the method of Thomas (10) by heating, if necessary, 132 g. of mercuric fluoride with 88 ml. of J. T. Baker Company bromoform and collecting the distillate. The distillate boiling below 80° was fractionated using a twelve inch glass column filled with tantalium helices at a reflux ratio of 10:1. The fraction boiling at 62.9° u. c. and 739 mm., had the following properties: $d_4^{27.7}$ 2.3533, $n_D^{28.6}$ 1.4624. Reported values are b.p. 64.9° at 757 mm., $d^{18.5}$ 2.4256 (11).

Sodium Hydroxide Solution.— Carbonate-free sodium hydroxide solution was prepared by the dilution of filtered 50 per cent sodium hydroxide with air-free distilled water, which was stored under nitrogen. The solution was standardized against potassium acid phthalate using phenolphthalein as an indicator. The solutions were stored in polyethylene bottles.

Hydrochloric Acid.— Hydrochloric acid was prepared by the dilution of

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10 C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953, p. 18.

11 F. Swarts, Chemisches Zentralblatt, 1910-I, 1868.

the C. P. 35 per cent acid, with distilled water. It was standardized with standard sodium hydroxide solution.

Salts.— All of the salts used were C. P. or U. S. P. and, with the exception of drying, were used without further purification. The solutions were prepared by dissolving a weighed amount of salt in air-free distilled water and stored under nitrogen. Sodium perchlorate was prepared from a stock solution of 3 M salt.

Dibromochloromethane.— The Dow Chemical Company haloform was washed three times with 5 ml. portions of sulfuric acid, followed with three 50 ml. portions of distilled water for every 100 ml. of haloform used. Distillation over phosphorus pentoxide yielded a product with the following properties: b. p. 114-115° C., $d_4^{28.7}$ 2.446 grams per ml., $n_D^{28.7}$ 1.5433. Jacobsen and Neumeister reported a boiling point of 118-120° C. (12).

Perchloric Acid.— The 70 per cent acid was diluted with distilled water and standardized against standard sodium hydroxide.

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12 O. Jacobsen and R. Neumeister, Ber., 15, 601 (1882).

CHAPTER IV

DISCUSSION OF RESULTS

From mechanism I, the carbon dihalide molecules may react with water molecules, hydroxide ions, and halide ions. The fraction of the carbon dihalide molecules which escapes reconversion to the original haloform can be written as:

$$F = \frac{k_w [H_2O] + k_h [OH^-]}{k_w [H_2O] + k_h [OH^-] + k_x [X^-]} \qquad (1)$$

or

$$F = \frac{[H_2O] + \frac{k_h}{k_w} [OH^-]}{[H_2O] + \frac{k_h}{k_w} [OH^-] + \frac{k_x}{k_w} [X^-]}$$

where k_w, k_h, and k_x are the specific second order rate constants for the reaction of carbon dihalide with water, hydroxide ion, and halide ion, respectively. If $\underline{k}$ represents the initial rate constant in the presence of a given concentration of a salt whose anion does not significantly combine with the carbon dihalide, and if $\underline{k}'$ represents that found in the presence of the same concentration of bromide and iodide ions, then

$$F = \frac{k'}{k} \qquad (2)$$

Solution of equations (1) and (2) for the competition factor k_x/k_w yields

$$\frac{k_x}{k_w} = \frac{\left([H_2O] + \frac{k_h}{k_w}[OH]\right)\left(\frac{k}{k'} - 1\right)}{X^-} \qquad (3)$$

The value of k_x/k_w can be evaluated at zero time if k'/k is found by extrapolation to zero time, and if the concentrations are known at zero time. Values of the competition factor will be measures of the relative ability of the ions to combine as nucleophilic agents with carbon dihalide. Swain and Scott (13) have developed the following equation to correlate the rates of reaction of various nucleophilic reactants with different substrates:

$$\log \frac{k_x}{k_w} = sn.$$

In this equation n is the specific nucleophilic constant for that reagent and s is a constant related to the substrate's ability to discriminate between various nucleophilic reagents. If k_w is small compared with k_{x1} and k_{x2} we may write:

$$\frac{\log k_{x1}}{\log k_{x2}} = \frac{n_1}{n_2} \qquad (4)$$

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13 C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (1953).

where n_1 and n_2 are specific nucleophilic constants. Swain and Scott give values of $\underline{n}$ as 3.89 ± 0.09, 4.20 ± 0.15, and 5.04 ± 0.21 for bromide, hydroxide, and iodide ions, respectively, as compared to 0.00 for water.

The average value of $\underline{k}$ for dibromochloromethane in the presence of the inert salts, sodium nitrate, sodium fluoride and sodium perchlorate, is 0.005601 liters per mole per second. The value of $\underline{k'}$ for dibromochloromethane in the presence of sodium iodide was found from extrapolating the data of Table 13 to zero time to be 0.0034. Thus, k/k' has a value of 1.647.

The value of $\underline{k'}$ for dibromochloromethane in the presence of sodium bromide at the same salt concentration is 0.004277 liters per mole per second. Thus, k/k' has a value of 1.3095.

The $[H_2O]$ has a value of 55.5 moles per liter.

Simultaneous solution of equations (3) and (4) for k_x/k_w for bromide, iodide, and hydroxide, leads to values of 209, 462, and 237, respectively. The value for the hydroxide ion is the average value found from solving the equations for bromide and iodide ions. Log k_x/k_w was calculated. The results are listed in Table 6.

Log k_x/k_w versus $\underline{n}$ should yield a straight line. To test the results, the data of Table 6 was plotted. The slope of the line is 0.55, thus, this is the value of $\underline{s}$ for bromochloromethylene. The parameter, $\underline{s}$, is related to the ability of the substate to discriminate between various nucleophilic reagents. It has been demonstrated that increasing ab-

ility of halide ions to compete with water for carbonium ions is found with increasing stability of the carbonium ions (14, 15). The value of s of 0.54 found for carbon dichloride by Hine and Dowell (1) is very close to the value for bromochloromethylene. It is reasonable to conclude that carbon dichloride and bromochloromethylene are of comparable reactivity towards simple nucleophilic reagents.

It is possible to rule out mechanism II and mechanism III on the basis of the results of the basic hydrolysis of dibromochloromethane in the presence of added salts.

From the data presented it is seen that the reduction in the rate of hydrolysis of dibromochloromethane in the presence of the added salts was of the order NaI > NaBr. Both of these rates are lower than the rate in the presence of an inert salt. In addition, the rate constant fell with time, in the presence of sodium iodide. These facts are consistent with the carbon dihalide mechanism, because a nucleophilic attack of the halide ion upon the carbon dihalide intermediate would be expected to reduce the over-all rate of hydrolysis of the haloform by reverting a part of the carbon dihalide to either dibromochlorocarbanion or chlorobromoiodocarbanion.

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14 L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, J. Chem. Soc., 1940, 979.

15 C. G. Swain, C. B. Scott and K. H. Lohmann, J. Am. Chem. Soc., 75, 136 (1953).

1 J. Hine and A. M. Dowell, Jr., J. Am. Chem. Soc., 76, 2688 (1954).

Table 6. Values of the Competition Factor for Halide Ions with Bromochloromethylene at 0.09 N Added Salt Concentrations.

Ion	N NaOH	k_x/k_w	log k_x/k_w	n
Bromide	0.020	210	2.32	3.89
Iodide	0.027	460	2.66	5.04
Hydroxide		240	2.37	4.20

Any intervention of the halide ion in mechanism III would be upon the intermediate trihalomethyl ion or the intermediate $H_2\overset{+}{O}-\overset{-}{C}X_2$. The S_N2 attack of bromide ion on the trihalomethyl intermediate should cause no change in the rate of hydrolysis of dibromochloromethane. The S_N2 attack of iodide on the dibromofluoromethyl carbanion would form a bromofluoroiodomethyl carbanion. The ratio of basic hydrolysis of dichlorobromomethane is about five times faster than dichloroiodomethane (9). It appears reasonable that the bromofluoroiodomethyl carbanion would react slower than the dibromofluoromethyl carbanion, and that the over-all rate of basic hydrolysis of dibromochloromethane could be slower in the presence of iodide ions than in the presence of neutral salts, if mechanism III represented the correct mechanism.

An attack of halide ions on $H_2\overset{+}{O}-\overset{-}{C}X_2$ does not appear likely in view of the low stability of such an intermediate in basic solution. As an oxonium ion, the intermediate would be subject to rapid loss of the proton, or rapid rearrangement to $HO-CHX_2$. The short life of the oxonium intermediate would not be expected to allow any specific effect of halide ions other than a general salt effect. Therefore, mechanism III may be ruled out.

A reversal of the first step in mechanism II appears unlikely because of the extreme difficulty of replacing a hydroxyl group by S_N2 at-

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9 A. M. Dowell, Jr., Ph. D. Thesis, Georgia Institute of Technology, 1954, p. 40.

tack, and because of the expected large reactivity of the $HOCHX_2$ intermediate. Mechanism II may be ruled out.

CHAPTER V

CONCLUSIONS

It has been demonstrated by the intervention of bromide ions and iodide ions that the basic hydrolysis of dibromochloromethane proceeds through a trihalomethyl carbanion and a carbon dihalide intermediate, and not through a S_N2 attack of water molecules upon a trihalomethyl anion, or through a S_N2 attack of hydroxide ions upon the haloform molecules. By the use of relative rate constants, the results of the interaction of halide ion with bromochloromethylene have been quantitatively correlated with the nucleophilicity constants for halide ions.

While any intervention of bromide ions and iodide ions upon the basic hydrolysis of dibromofluoromethane was of less magnitude than the experimental error, the predicted rate of carbanion formation of the haloform and considerations of other possible mechanisms show that the basic hydrolysis probably proceeds through a trihalomethyl anion and a carbon dihalide intermediate.

The relative order of reactivity toward sodium hydroxide was found to be:

$$CHBr_2F > CHBr_2Cl > CHBrClI.$$

CHAPTER VI

RECOMMENDATIONS

Mechanism I requires that the rate of carbanion formation of the haloforms in basic solution be faster than the hydrolysis rate. The hydrolysis rate of dibromochloromethane at 40.0° C. is 0.005601 liters per mole per second in the presence of 0.08 N neutral salt. The deuterium exchange rate should be larger than 0.0056 liters per mole per second.

The hydrolysis rate of dibromofluoromethane at 0.0° C. is 0.00278 liters per mole per second in the presence of 0.08 N neutral salt. The deuterium exchange rate of dibromofluoromethane has been predicted to lie between 0.0036 and 0.0054 liters per mole per second.

If the deuterium exchange rates are found to be greater than the hydrolysis rates, mechanism I will be more strongly established.

Since the lowering of the hydrolysis rates of dibromofluoromethane by the bromide and iodide ions was within the experimental error at the salt concentrations used, a repetition of the experiment with stronger salt concentrations may bring out the specific effects of bromide and iodide ions on the rate constant.

APPENDIX

Table 7. Dibromofluoromethane in the Presence of 0.08 N Sodium Fluoride.

Time Seconds	Delta Titer ml.	$k \times 10^6$ liters per mole per second	$k_o \times 10^5$ liters per mole per second
0	3.12		
78	3.79	3336	268
138	4.05	3327	268
373	5.48	3300	273
379	6.19	3479	288
1105	9.54	3579	315[c]
3457	15.33	3030	285
Average			276 ± 8

a = 0.03090 b = 0.03573 f = 0.536

Infinite delta titer 22.32 ml. of 0.1786 N NaOH

Acid - 25 ml. of 0.15840 N HCl

Reaction volume - 100 ml.

[c]Not averaged.

Table 8. Dibromofluoromethane in the Presence of 0.08 N Sodium Nitrate.

Time Seconds	Delta Titer ml.	$k \times 10^6$ liters per mole per second	$k_o \times 10^5$ liters per mole per second
00	3.21		
62	3.70	3865	304
221	4.80	3688	299
308	5.41	3746	315
357	5.63	3585	296
420	5.94	3479	289
558	6.71	3460	295
856	8.13	3365	281
1153	9.38	3238	285
1455	10.58	3323	289
1697	11.22	3201	298
2223	12.97	3280	302
2290	12.90	3148	290
2802	14.17	3150	293
4619	17.11	3043	291
Average			295 ± 6

a = 0.03100 b = 0.03573 f = 0.536

Table 8. Dibromofluoromethane in the Presence of 0.08 N Sodium Nitrate.

(cont.)

Infinite delta titer 22.32 ml. of 0.1786 N NaOH

Acid - 25 ml. of 0.1584 N HCl

Reaction volume - 100 ml.

Table 9. Dibromofluoromethane in the Presence of 0.08 N Sodium Bromide.

Time Seconds	Delta Titer ml.	$k \times 10^6$ liters per mole per second	$k_o \times 10^5$ liters per mole per second
0	3.16		
920	8.09	3125	272
1218	9.31	3135	278
1774	11.11	3039	275
2547	12.69	2768	258[c]
4117	16.13	2947	280
Average			276 ± 3

a = 0.03077 b = 0.03573 f = 0.536

Infinite delta titer 22.32 ml. of 0.1786 N NaOH

Acid - 25 ml. of 0.1584 N HCl

Reaction volume - 100 ml.

[c]Not averaged.

Table 10. Dibromofluoromethane in the Presence of 0.08 N Sodium Iodide.

Time Seconds	Delta Titer ml.	$k \times 10^6$ liters per mole per second	$k_o \times 10^5$ liters per mole per second
0	5.56		
532	8.54	3170	267
1126	11.20	3057	264
1855	13.56	2953	268
2224	14.46	2877	265
3414	17.09	2861	268
3984	17.94	2801	265
Average			266 ± 2

a = 0.03077 b = 0.03573 f = 0.536

Infinite delta titer 22.32 ml. of 0.1786 N NaOH

Acid - 25 ml. of 0.1584 N HCl

Reaction volume - 100 ml.

Table 11. Dibromofluoromethane in the Presence of 0.08 N Sodium Perchlorate.

Time Seconds	Delta Titer ml.	$k \times 10^6$ liters per mole per second	$k_o \times 10^5$ liters per mole per second
0	0.61		
1725	6.15	3190	277
1890	4.80	3110	281
2210	8.22	2981	274
2910	9.44	2930	273
3705	10.67	2982	280
Average			277 ± 3

a = 0.03541 b = 0.05212 f = 0.536

Infinite delta titer 20.52 ml. of 0.3301 N NaOH

Acid - 20 ml. of 0.3387 N $HClO_4$

Reaction volume - 95 ml.

Table 12. Dibromochloromethane in the Presence of 0.09 N Sodium Iodide.

Time Seconds	Delta Titer ml.	k x 10^6 liters per mole per second
0	12.54[d]	
575	13.80[d]	3356
660	13.93[d]	3243
1775	16.08[d]	3447
2570	0.98[c]	3239
3765	18.57[d]	3183
6685	4.62[c]	2818
10660	6.06[c]	2633
10735	6.84[c]	2657
13840	7.73[c]	2422
Extrapolated to zero time		3400

a = 0.01110 b = 0.02744 f = 0.164

[c]Infinite delta titer 16.14 ml. of 0.1168 N NaOH

Acid - 10 ml. of 0.1886 N $HClO_4$

[d]Infinite delta titer 32.28 ml. of 0.1168 N NaOH

Acid - 20 ml. of 0.1886 N $HClO_4$

Reaction volume - 90 ml.

Table 13. Dibromochloromethane in the Presence of 0.09 N Sodium Fluoride.

Time Seconds	Delta Titer ml.	$k \times 10^{-4}$ liters per mole per second
0	3.55	
1233[d]	5.20	[e]
1842[d]	6.04	5284
3565[d]	7.64	5617
10800[c]	2.00	5522
14400[c]	2.60	5253
Average		5419 ± 148

a = 0.01058 b = 0.01984 f = 0.164

[c]Infinite delta titer 4.44 ml. of 0.1786 N NaOH

Acid - 5 ml. of 0.1586 N $HClO_4$

[d]Infinite delta titer 13.32 ml. of 0.1786 N NaOH

Acid - 15 ml. of 0.1586 N $HClO_4$

Reaction volume - 90 ml.

[e]Not averaged.

Table 14. Dibromochloromethane in the Presence of 0.09 N Sodium Fluoride.

Time Seconds	Delta Titer ml.	k x 10^{-6} liters per mole per second
0	3.56	
260	4.02	5707
887	5.07	5982
3413	7.92	[c]
4382	8.44	5803
7455	10.01	5830
Average		5830 ± 76

a = 0.01058 b = 0.01984 f = 0.164

Infinite delta titer 13.32 ml. of 0.1786 N NaOH

Acid - 15 ml. of 0.1586 N $HClO_4$

Reaction volume - 90 ml.

[c]Not averaged.

Table 15. Dibromochloromethane in the Presence of 0.09 N Sodium Bromide.

Time Seconds	Delta Titer ml.	$k \times 10^{-6}$ liters per mole per second
0	3.55	
735	4.48	4346
1283	5.12	4262
1965	5.88	4419
2642	6.39	4309
3032	6.56	4051
Average		4277 ± 50

a = 0.01058 b = 0.01984 f = 0.164

Infinite delta titer 13.32 ml. of 0.1786 N NaOH

Acid - 15 ml. of 0.1586 N $HClO_4$

Reaction volume - 90 ml.

Table 16. Dibromochloromethane in the Presence of 0.09 N Sodium Perchlorate.

Time Seconds	Delta Titer ml.	$k \times 10^{-6}$ liters per mole per second
0	0.63	
561	1.57	5448
980	2.18	5502
1870	3.36	5672
4208	5.27	5437
7340	7.06	5729
10800	6.85	5596
16905	8.98	5194
Average		5511 ± 98

a = 0.01060 b = 0.01997 f = 0.164

Infinite delta titer 10.48 ml. of 0.1797 N NaOH

Acid - 10 ml. of 0.1883 N $HClO_4$

Reaction volume - 90 ml.

Table 17. Dibromochloromethane in the Presence of 0.09 N Sodium Nitrate.

Time Seconds	Delta Titer ml.	$k \times 10^{-6}$ liters per mole per second
0	3.55[c]	
5376	8.92[c]	5602
7196	0.88[d]	5567
10719	1.87[d]	5288
Average		5486 ± 19

a = 0.01058 b = 0.01984 f = 0.164

[c]Infinite delta titer 13.32 ml. of 0.1786 N NaOH

Acid - 15 ml. of 0.1883 N $HClO_4$

[d]Infinite delta titer 4.44 ml. of 0.1786 N NaOH

Acid - 5 ml. of 0.1883 N $HClO_4$

Reaction volume - 90 ml.

Table 18. Dibromochloromethane in the Presence of 0.09 N Sodium Nitrate.

Time Seconds	Delta Titer ml.	$k \times 10^{-6}$ liters per mole per second
0	.61	
582	1.68	6123
809	2.45	[c]
2351	3.12	6041
2975	4.58	5989
3567	5.04	5266
Average		5854 ± 295

a = 0.01064 b = 0.01984 f = 0.164

Infinite delta titer 10.48 ml. of 0.1797 N NaOH

Acid - 10 ml. of 0.1883 N $HClO_4$

Reaction volume - 90 ml.

[c]Not averaged.

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PART II

AN ATTEMPTED SYNTHESIS OF

CYCLOBUTENE

CHAPTER I

INTRODUCTION

Ramberg and Backlund (1) have reported the following reactions:

$$CH_3CH_2SO_2CHBrCH_3 + 3KOH \rightarrow \text{cis-}CH_3CH{:}CHCH_3 + KBr + K_2SO_3 + 2H_2O \quad (1)$$

$$CH_3CH_2SO_2CHBrCH_2CH_3 + 3KOH \rightarrow CH_3CH{:}CHCH_2CH_3 + KBr + K_2SO_3 + 2H_2O$$

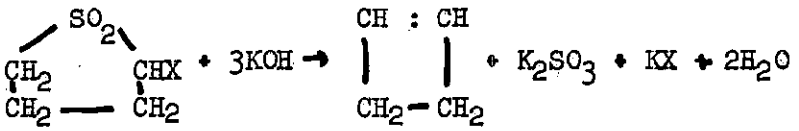
Bordwell and Cooper (2) have reported:

$$C_6H_5CH_2SO_2CH_2Cl + 3KOH \rightarrow C_6H_5CH{:}CH_2 + K_2SO_3 + KCl + 2H_2O$$

$$C_6H_5CHClSO_2CH_3 + 3KOH \rightarrow C_6H_5CH{:}CH_2 + K_2SO_3 + KCl + 2H_2O$$

$$C_6H_5CH_2SO_2CHClC_6H_5 + 3KOH \rightarrow \text{trans-}C_6H_5CH{:}CHC_6H_5 + K_2SO_3 + KCl + 2H_2O$$

If an alpha-halotetramethylene sulphone were to undergo a similar reaction,



$$+ 3KOH \rightarrow \quad + K_2SO_3 + KX + 2H_2O \qquad (2)$$

and if the halotetramethylene sulphone were sufficiently available, the

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1 L. Ramberg and B. Backlund, Arkiv. Kemi Mineral. Geol., 13A, No. 27, 50 (1940).

2 F. G. Bordwell and G. D. Cooper, J. Am. Chem. Soc., 73, 5187 (1951).

reaction might represent the best known synthesis of cyclobutene. The mechanism of reaction 1 involves three steps (2):

$$CH_3CH_2SO_2CHXCH_3 + OH^- \rightleftharpoons CH_3\dot{C}HSO_2CHXCH_3 + H_2O \qquad \text{(fast)}$$

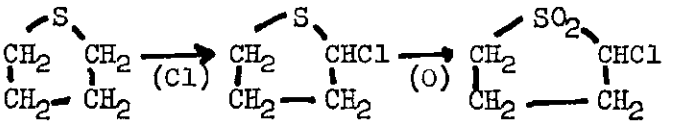
$$CH_3\dot{C}HSO_2CHXCH_3 \rightleftharpoons CH_3\overbrace{CHSO_2}CHCH_3 + X^- \qquad \text{(slow)}$$

$$CH_3\overbrace{CHSO_2}CHCH_3 \xrightarrow[OH^-]{} H_2O + SO_3^{=} + CH_3CH{:}CHCH_3 \qquad \text{(fast)}$$

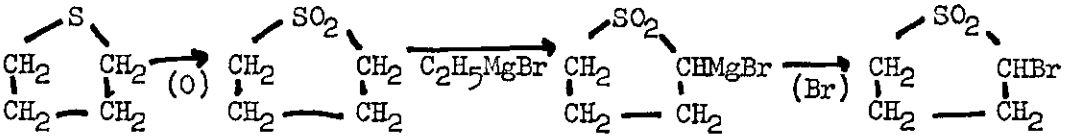
This mechanism and the cis-configuration of the final product lends support to the belief that reaction 2 is possible.

A search of the literature revealed that an alpha-halotetramethylene sulphone has not been reported. The synthesis of an alpha-halotetramethylene sulphone from either of the following syntheses appeared promising:

Synthesis I



Synthesis II



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2 F. G. Bordwell and G. D. Cooper, J. Am. Chem. Soc., 73, 5187 (1951).

The present study was undertaken to see if synthesis I or II could produce an alpha-halotetramethylene sulphone in sufficient quantities to attempt reaction 2.

A search of the literature, when synthesis I was begun, showed that no halogenations of thiophane had been attempted. Halogenations of other thioethers have been reported to give alpha-halo-derivatives (3, 4, 2). The oxidation of thiophane to tetramethylene sulphone is well known. No halogenations or Grignard-halogenations of tetramethylene sulphone had been found in the literature.

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2 F. G. Bordwell and G. D. Cooper, J. Am. Chem. Soc., 73, 5187 (1951).

3 W. E. Truce, G. H. Birum, and E. T. McBee, J. Am. Chem. Soc., 74, 3594 (1952).

4 H. Bohme, Ann., 577, 68 (1952).

CHAPTER II

PROCEDURE

Synthesis I

Thiophane.— Thiophane was prepared by the method of Braun and Trumpler (5) with the following modifications: sodium sulphide and 1,4-dichlorobutane were used in place of potassium sulphide and dibromobutane, respectively. Ethylene glycol was used as the solvent since it can easily be separated from the product due to its high boiling point. In a three-liter flask fitted wth a reflux condenser, 1.460 g. (6.1 moles) of Merck reagent sodium sulphide nonohydrate, 400 ml. of ethylene glycol, and 744 g. (5.85 moles) of Du Pont technical 1,4-dichlorobutane were refluxed twenty hours. The mixture was fractionated. The fraction 88-116° was collected. The thiophane layer was removed from the aqueous layer in a separatory funnel and dried over calcium chloride. The 385 ml. of crude thiophane was fractionated. A total of 260 ml. of azeotrope, consisting of 96 per cent thiophane and 4 per cent dichlorobutane was collected at 120.0-121.5°. The yield was 49 per cent thiophane.

Chlorination of Thiophane with Chlorine Gas.— A 500 ml. three-neck flask containing 47.4 g. (0.35 moles) of thiophane dissolved in 139.9 g. of car-

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5 J. von Braun and A. Trumpler, Ber., 43, 550 (1910).

bon tetrachloride, which was dried over calcium chloride, was fitted with a reflux condenser, a thermometer and a fritted gas dispersion tube leading to a cylinder of chlorine gas. The end of the condenser was connected to a drying tube filled with calcium chloride. The flask was surrounded with a bath of acetone cooled to -28° by pellets of dry ice. Over a period of ninety minutes, 29 g. (0.41 moles) of chlorine gas was passed into the solution. Two liquid phases were visible. After standing fifteen minutes in room temperature, the upper cloudy layer became a dark brown. A gas which fumed in the air was discharged from the drying tube. The liquid was refluxed for one hour at 45-50°. Most of the low boiling components were removed with a water aspirator. The remaining liquid was fractionated at a pressure of 20 mm. of mercury. About 40 ml. of liquid, believed to be carbon tetrachloride and thiophane, was collected at 58-61°. The dark, viscous syrup remaining in the flask did not distill at 105° and 3 mm. of mercury.

Chlorination of Thiophane with Sulfuryl Chloride.— A 500 ml. three-neck flask was fitted with a 200 ml. separatory funnel, a thermometer, and a reflux condenser, connected to a calcium chloride drying tube. After being placed in an acetone bath cooled to -35° with dry ice pellets, the flask was filled with 44 g. (0.48 moles) of thiophane. Over a period of two hours 75 g. (0.55 moles) of Baker Company sulfuryl chloride was run into the thiophane. The clear, yellow liquid was allowed to reach room temperature. At -7° the solution became black and opaque. The solution

was warmed to 34° and held at this temperature for one hour until no gasses were being evolved. The liquid was distilled at 40-50 mm. of mercury. Three milliliters of liquid believed to be impure thiophane was collected at 40-42°. The dark liquid left in the flask did not distill at a temperature of 189°. The dark liquid was identical in appearance to the tarry liquid produced by direct chlorination of thiophane.

Chlorination of Thiophane with Thionyl Chloride.— The apparatus described above was used for the chlorination. The same procedure was followed with 66 g. (0.55 moles) of thionyl chloride in place of the sulfuryl chloride. After addition of thionyl chloride the flask was allowed to reach room temperature. Gasses were being evolved and the reaction mixture became darker. No attempt was made to separate the desired product from the material in the reaction flask.

Synthesis II

Tetramethylene Sulfone.— In a three-liter flask fitted with a reflux condenser, 57.5 g. (0.63 moles) of thiophane and 250 ml. of Du Pont glacial acetic acid were mixed. Through the top of the condenser, 260 ml. of 35 per cent hydrogen peroxide were added drop by drop for one hour. The flask was carefully heated at 75° for two hours. A higher temperature caused a violent reaction. The flask was then placed in a steam bath. At the end of one hour, the reflux condenser was replaced with a line leading to a water aspirator and the volatile portion of the liquid

was boiled off. The remaining 50 ml. of liquid was fractionated under a vacuum of 10.5-11.0 mm. of mercury. The fraction boiling at 140.5-141.0° was collected. The yield was 61.2 g. or 74 per cent of tetramethylene sulfone. The product had a density of 1.273 at 30°. E. Grishkevich-Trokhimivskii reports $d_4^{18.2}$ 1.2723, and b. p.$_{18}$ 153-154° (6).

Attempted Bromination of Tetramethylene Sulfone.—The method used by Ziegler and Connor (7) for the bromination of methyl p-tolyl sulfone was followed. A 500 ml. three-neck flask was fitted with a stirrer, dropping funnel, and a reflux condenser, connected to a drying tube filled with calcium chloride. Over a period of thirty minutes 75 ml. of 0.2 N ethyl magnesium bromide in ethyl ether was added dropwise to 18.7 g. (0.156 moles) of tetramethylene sulfone dissolved in 100 ml. anhydrous ether. The addition was accompanied with the evolution of gasses and a slight amount of heat. A voluminous white-gray solid was present in the liquid. One hundred milliliters of sodium-dried benzene was added. The solution was refluxed for three minutes and then cooled in an ice bath. Over a period of thirty minutes 24 g. (0.146 moles) of Dow Chemical Company technical bromine in 50 ml. anhydrous benzene was added. A sticky orange lump replaced the white-gray solid.

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6 E. Grishkevich-Trokhimivskii, J. Russ. Phys. Chem. Soc., 48, 901-928 (1916).

7 W. M. Ziegler and R. Connor, J. Am. Chem. Soc., 62, 2598 (1940).

The liquid was decanted and evaporated. A white solid remained. The solid was insoluble or slightly soluble in petroleum ether, chloroform and benzene, and soluble in water and ethanol. An aqueous solution of the solid, produced a yellow precipitate and a gelatinous precipitate when treated with silver nitrate solution and sodium hydroxide solution, respectively. A white residue remained after ignition. The solid was assumed to be magnesium bromide.

The taffy-like solid in the flask was dissolved in 200 ml. of water and 50 ml. of benzene. The water and benzene were evaporated with the aid of a fan. The remaining oil and solid were mixed with 200 ml. of benzene. The benzene solution was decanted and evaporated. The remaining 5 to 10 ml. of oil was dried over calcium sulfate, and fractionated in a Hickman vacuum still. A pressure of 0.001-0.003 mm. of mercury was obtained using a 2-ethyl hexyl phthalate diffusion pump backed by a two-cycle oil pump. The Hickman still was heated by an oil bath. Two fractions were obtained. Due to difficulties in controlling the temperature of the still bath and lack of a means of determining the vapor temperature, the exact boiling range of each fraction is unknown. The maximum temperature of the bath was 72°. The low-boiling, high-boiling and still fractions of the bath occupied 4.0, 0.3, and 0.5 ml., respectively.

The low-boiling fraction had a refractive index of 1.4870 at 30°. A sodium fusion test was applied to a portion of this fraction. The carbon tetrachloride-chlorine test for bromine was negative. The silver ni-

trate test for halide ion was inconclusive.

The high-boiling fraction had a density of 1.230 and a refractive index of 1.4875 at 30°. A molecular weight determination by Rast's camphor method led to a molecular weight of 233. Due to some loss of camphor by sublimation, the molecular weight is believed to be low. The molecular weight of alpha-bromotetramethylene sulfone is 200. The molecular weight of tetramethylene sulfone is 120. A tetramethylene sulfone dimer has a molecular weight of 240. An infra-red spectrum of this fraction was identical with the spectrum of pure tetramethylene sulfone. This work suggests that tetramethylene sulfone exists as a dimer.

The slightly yellow color of the liquid in the still was believed to be due to a small amount of magnesium bromide impurity. No tests were performed on this fraction.

CHAPTER III

DISCUSSION OF RESULTS

The product obtained from the chlorination of thiophane was black, tarry syrup with a high boiling point. The physical properties of the product suggest that any alpha-halotetramethylene sulfide formed polymerized. Since thioethers add to alkyl halides and since a halotetramethylene sulfide molecule has properties of both a thioether and an alkyl halide, two or more alpha-halothiophane molecules could combine to form a high molecular weight product. After synthesis I had been completed, Bordwell and Pitt reported that the chlorination of thiophane with sulfuryl chloride yielded a resinous product together with small quantities of low-boiling products with a wide boiling point range (8).

Synthesis I was abandoned as a satisfactory method for obtaining sufficient quantities of an alpha-halotetramethylene sulfone to attempt reaction 2.

The molecular weight of 233 determined from Rast's camphor method indicated that tetramethylene sulfone exists as a dimer.

There was no detectable product found after the Grignard-Bromination of tetramethylene sulfone. A search of the literature revealed that

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8 F. G. Bordwell and B. M. Pitt, J. Am. Chem. Soc., 77, 576 (1955).

diethyl sulfone was found to be unreactive with chlorine gas (9) and phosphorous pentachloride (10). Since tetramethylene sulfone is structurally similar to diethyl sulfone, it is reasonable to find that tetramethylene sulfone is also unreactive to Grignard-Bromination. The evolution of a gas, probably ethane, the liberation of heat and the formation of a precipitate, when ethyl magnesium bromide was added to an ether solution of tetramethylene sulfone, could be attributed to trace impurities of water in the reagents or to water in the atmosphere above the solutions in the reaction flask. Since no detectable yield was obtained, synthesis II was considered unsuitable for the production of an alpha-halotetramethylene sulfone.

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9 W. Spring and C. Wissinger, Ber., 15, 446 (1882).

10 A. von Oefele, Ann. 132, 90 (1864).

CHAPTER IV

CONCLUSIONS

Two different unsuccessful syntheses of an alpha-halotetramethylene sulfone were attempted. The first method was abandoned when it was found that the chlorination product of thiophane was a high-boiling, tarry liquid, probably a polymer of chlorothiophane. The second synthesis was abandoned when Grignard-Bromination of tetramethylene sulfone produced no detectable product.

Since both syntheses failed to produce sufficient alpha-halotetramethylene sulfone, reaction 2 could not be tried.

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